

Weathering of Low-Density Polyethylene Grafted with Itaconic Acid in Laboratory Tests

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ABSTRACT: Polyethylene grafted with itaconic acid was subjected to weathering under laboratory accelerated conditions. The course of the photo-oxidative degradation process of that material was studied by FTIR spectroscopy both through quantitative measurements of changes in absorbance values at selected wave numbers and through measurements of surface area values for absorption bands which were separated by means of deconvolution. The use of both those procedures of quantitative determinations resulted in a general conclusion that the oxidation process was initiated from the very first moment of irradiation,

and it produced ketones, acids, esters (intramolecular and of acetate type), peracids, peresters, hydroperoxides, and alcohols. The molecular weight values and gel number values, which were established as well, pointed out that oxidation was accompanied by cracking of polymer macromolecules, and also by polymer crosslinking to a limited degree. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1634–1642, 2012

Key words: polyethylene; itaconic acid; ageing; FTIR; polymer structural changes

INTRODUCTION

The polymers have been winning the global markets for a few decades and have been strengthening their positions in numerous branches of economy. The global consumption trends indicate clearly that polyolefins enjoy the highest popularity, and polyethylene (PE) makes the market leader. Since PE is cheap, chemically inactive—hence nontoxic, easy to process, and offers high electrical resistance, it makes the most frequently used polymer in the world nowadays. Its physical properties can be adjusted over a wide span by changing parameters of its production process. The list of its drawbacks, from the viewpoint of numerous applications, comprises low endurance under continuous load conditions, no stability at high temperatures, and relatively low softening point. Also, its low reactivity (resulting from no functional groups) reduces PE compatibility with numerous other materials and its dyeability. PE is for that reason subjected to various physical and chemical modification processes (crosslinking, oxidation, and functionalization reactions). Depending on specific needs, those changes may involve the bulk of the polymer or its surface only (with the bulk properties intact).

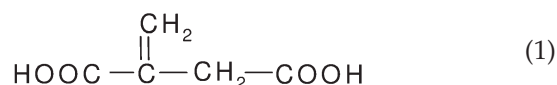
The functionalization (grafting) reactions have been intended to bond molecules of selected chemical compounds which contain functional groups to the polymer chain. The purpose of those reactions^{1–3} is to improve adhesion of the polymer to metals and other polar materials, to improve its dyeability, wettability with liquids and/or resistance to thermal oxidation, light ageing, and also to prevent extraction of a modifying agent, especially a polar one, which is not chemically fixed. Finally, it seems feasible to improve the polymer degradability with the use of the modification method as mentioned here.

Itaconic acid (IA) is one of numerous compounds which can be grafted onto macromolecules of PE and other polyolefins.^{4–10} Little attention has so far been paid in the reports to the problem of resistance of such copolymers to degradation, e.g., due to sunlight or elevated temperature. The article by Pesetskii et al. on oxidation in water of PE grafted with IA makes an exemption to that rule.¹¹ The knowledge on whether a polymer is sensitive to various environmental impacts and service conditions or not is yet essential when defining outlets and application conditions for a material, the more so because polymers are readily employed in many outdoor applications.¹² Under such service conditions, they usually undergo photo-oxidative degradation with the formation of oxygen-containing groups, principally carbonyl groups. The research has revealed^{13–15} that it is just the stage of abiotic degradation (change in chemical structures of macromolecules) to be decisive

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for the rate of possible further biodegradation of PE in the natural environment, and the higher amounts of abiotic oxidation products enhance biodegradability of that polymer. Bio-erosion was noticed to be responsible for removal of PE oxidation products, mainly carboxylic acids and esters, from the bulk of the polymer. Moreover, the produced carboxylic acids may finally undergo oxidation to CO₂ and H₂O, even in the absence of micro- and/or macro-organisms.¹⁶

The purpose of our research was to analyze the weathering process of PE modified with IA [eq. (1)].



The first stage of the research program covered modification of low-density polyethylene (LDPE) with IA, by the reactive extrusion method. The obtained material, in the form of film, was then subjected to atmospheric (photo-oxidative) ageing under laboratory conditions, in a Xenotest weathering instrument. The polymer ageing advancement was observed on the basis of structural changes in the polymer macromolecules.

EXPERIMENTAL

Materials

The experiments involved low density PE, grafted with IA in the presence of dicumyl peroxide (DCP). The initial blend for modification contained 5 wt % of IA and 0.3 wt % of DCP. PE was modified with IA in a two-step extrusion process. The components were subjected to homogenization at the first step in a single-screw extruder, at 120°C. The produced melt was cooled down with water and granulated, and then it was dried in a laboratory drier, at (50 ± 5)°C, for 1 day.

The obtained mixture was subjected to reactive concurrent extrusion at about 200°C (in a twin-screw extruder, model BTSK from Bühler, with the screw diameter $D = 20$ and $L/D = 40$) at the second stage. For the screw rotational speed of 20 rev/min, the reaction time was about 3.7 min. The grafting degree for IA amounted to 4.5 wt %. The product melt flow index was 2.2 g/10 min at 120°C. The material also offered good mechanical properties: ultimate elongation $\varepsilon_B = 420\%$, and true tensile stress $\delta_B = 10$ MPa. The grafting degree was determined on the basis of the water extraction results for free IA (IA is well-soluble in water) that were presented in Ref. 17. Each tested sample in the form of molded piece, which was about 0.1 ÷ 0.3 mm thick, was cut into small fragments. The sample was weighed and the modifier which was unbound to the polymer was

recovered by extraction in boiling water over 5 h. The sample was then dried for 48 h at 50°C to constant mass. The grafting degree was calculated from the formula (2), where the weight of grafted monomer is the difference between the weight of the modifier added to the sample and the weight of its part which was extracted.

$$\text{DG} (\%) = \frac{m_i}{m_p} \times 100 \% \quad (2)$$

where: m_i —weight of grafted monomer in 100 g of compound, m_p —initial weight of PE in 100 g of compound.

Laboratory weathering test

The laboratory weathering test was conducted with the use of a light exposure and weathering testing instrument (Xenotest Alpha HE from Atlas, Germany). The test specimens in the form of film strips, 135 mm × 10 mm and about 0.2 mm thick, were placed in the frames of the specimen holder inside the test chamber and exposed to UV radiation. To obtain the best representation of the solar spectrum, filters were employed to cut off the range of wavelengths below 300 nm and to absorb the IR range. Each test cycle took 120 min and it was composed of a “light phase” (102 min) and a “dark phase” (18 min). During the “dark phase,” the xenon lamp was turned off and water was sprinkled over the test specimens to simulate rainfall. Irradiance for the “light phase” was adjusted at 80 W/m², temperature at 35°C, and humidity at 50%. The test stage termination criterion was based on UV radiation doses, which were established as: 15, 30, 45, 60, 80, 100, and 120 MJ/m², and which were equivalent to the actual weathering time of: 52, 104, 156, 208, 278, 347, and 417 h, respectively.

Evaluation of ageing progress

The progress of the laboratory weathering process was analyzed on the basis of structural changes (observed by IR spectrophotometry), molecular characterization (high-temperature gel chromatography method), and crosslinking index (analysis for gel number).

The IR spectral investigations were carried out with the use of a FTIR spectrometer (model PU 9804 from Philips Analytical, UK) and software EAGLE v. 4.1. The transmission spectra were recorded within 4000–400 cm⁻¹ with the resolution $R = 2$ cm⁻¹.

Since the shape of the absorption band was much complex within the “carbonyl range” due to overlapping absorption bands which represented various types of carbonyl groups, like acids, ketones, esters, peresters, and peracids, digital spectral separation

TABLE I
Specification of Absorption Bands in FTIR Spectra of Polyethylene Grafted with Itaconic Acid

Band frequency, wave number (cm ⁻¹)	Type of vibrations of chemical functionality	Type of functional groups and structural fragments
1712	STR C=O _{AC}	Free carboxylic acids C(O)OH
1695–1710	STR C=O...H _{AC}	Carboxylic acids bridged by hydrogen bonds
1630	STR C=C	Unsaturation or double bonds
1410	DEF CH ₂ (C ⁱ) _{AC}	Methylene groups at carbonyl acid carbon atoms CH ₂ C=O
1310	DEF OH _{AC}	Deformations of hydroxyl groups in acids
1216	STR/A C—C—O	C—C(O)—O groups in acids
1170	STR/S C—C—O	C—C(O)—O groups in acids
989	STR C—O	C—O bond in carboxylic acids
916	WAG OH...O _{AC}	Wagging vibrations in dimers of bounded acids
Doublet 830, 816	WAG =CH ₂	Vinylidene group of itaconic acid
Doublet 719, 730	RK(CH ₂) _n	Rocking vibrations of CH ₂ in polyethylene amorphous (719) and crystalline (730) phases

was conducted within 1870–1600 cm⁻¹. The deconvolution method and the software Grams v. 3.01B were employed to obtain individual spectral bands.

Molecular weights of polymers were determined with the use of the high-temperature gel chromatography method (GPC). The model 150C High Temperature Liquid Chromatograph from Waters (USA) was used for that purpose. The measurements were taken at 142°C and at the solvent flow rate of 1 cm³/min. The samples were dissolved in 1,2,4-trichlorobenzene (0.25 g/cm³) which was stabilized with Santonox-R. Polystyrene standards were used for calibration. The recorded results make the average of at least two measurements.

The crosslinking index (gel number) was found from gravimetric determination of the gel content in sample films which were subjected to extraction in boiling xylene during 5 h. Before boiling, each sample was weighed (*m*₁). That part of the tested material which was not dissolved (i.e., gel) was recovered by hot filtration and dried at 80°C ± 5°C over 24 h. Then it was weighed (*m*₂) again. The data were used to calculate the gel number (GN) by the mathematical formula (3):

$$\text{GN} = \frac{m_2}{m_1 - m_2} \times 100 \quad (3)$$

The recorded values make the average of at least two determinations. The analytical procedure was carried out before ageing and it was then repeated after the ageing test was completed.

The density values of polymers were measured with the use of a hydrostatic balance. Samples in the form of films were weighed to find their weights in air (*A*). They were then placed in water, at known temperature (and density— ρ_0), and they were weighed again (*B*). The data were used to calculate the sample densities (ρ) by the mathematical formula (4):

$$\rho = \frac{A}{A - B} \times \rho_0 \quad (4)$$

The measurements were taken with the use of an attachment unit to the AG204 balance (Mettler-Tolledo, Switzerland).

RESULTS AND DISCUSSION

Structural changes in tested samples (FTIR)

The results of the spectrophotometric FTIR analysis of the samples after their weathering made the basic tool for evaluation of the advances of the ageing process in PE grafted with IA. At the initial reference point, the material was subjected to characterization before its exposure to UV radiation. Individual bands in spectra were identified as presented in Table I.

Figure 1(a–c) represent the changes which were recorded during the weathering tests in the spectra of tested sample, for various ranges of wave numbers. The basic bands observable in the spectra of the polymer material over its ageing process are characterized in Table II and Figure 2 illustrates changes in intensities of bands which are specific in the presented spectra, *versus* weathering time.

Initially, lowering absorption values were observed in the test within the bands identified as representing free IA in the tested materials, and located at the wave numbers 1630, 1310, 1216, 1170, 989, 944, 916, 830, and 817 cm⁻¹. At the same time, the peak value of the principal band for the acid-type carbonyl groups was observed to shift gradually from the initial location at 1710 to the final location at 1715 cm⁻¹. That process took a few dozen hours of weathering [Fig. 1(a)] with no significant changes in the intensity of the band [Fig. 2(a)]. It should be noted that the intensity of the carbonyl band was highest within all analyzed bands over the whole period of a weathering test. Additionally, a local peak disappeared within that band, located at

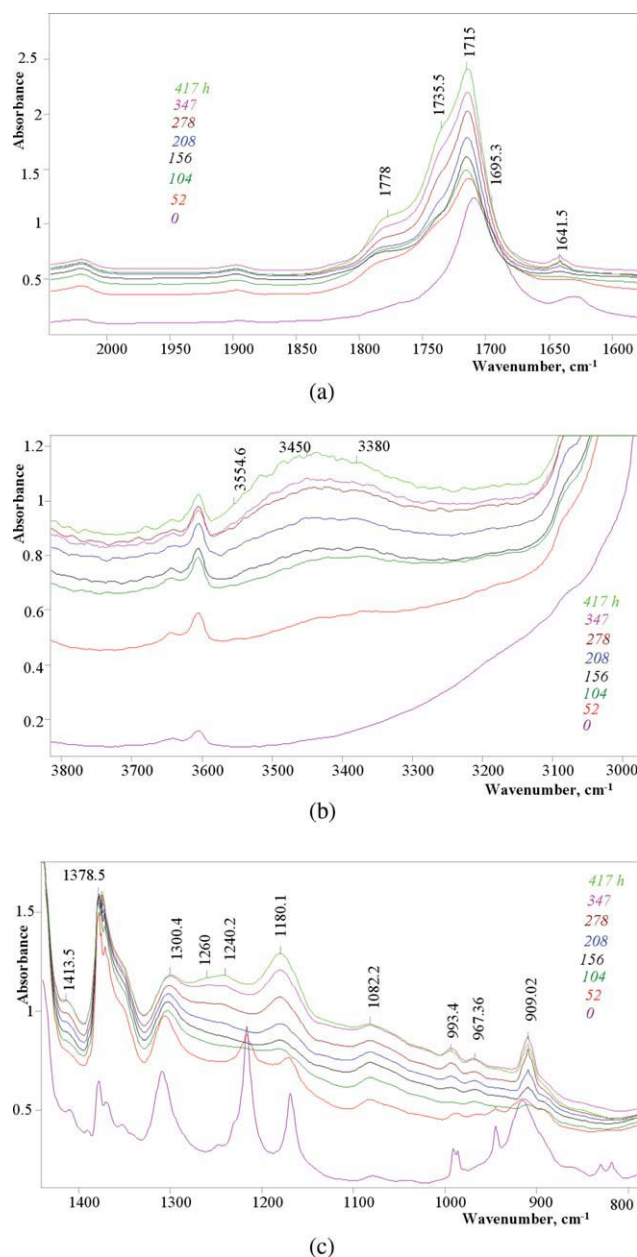


Figure 1 Changes in absorbances *versus* photo-oxidative ageing time, for bands representing: (a) carbonyl groups 2000–1600 cm^{-1} , (b) hydroxyl groups 3800–3000 cm^{-1} , (c) fingerprint range: 1415–800 cm^{-1} , in tested sample of PE grafted with IA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

about 1695 cm^{-1} ; it represented acids which were fixed with hydrogen bonds, or it could also represent C=O coupled on C=C in IA.

When interpreting changes observed within the spectrum, especially within the carbonyl band, one must take into consideration both those changes which may take place within polar groups derived from IA, and those which result from the oxidation process of the hydrocarbon chains in macromolecules of the polymer tested. As regards the first possibility, we may expect that UV radiation converted

that part of IA which had not been bonded earlier to PE chains in reactive processing. The changes were likely to take place within the unsaturated bond $\text{CH}_2=\text{C}$ in the acid structure, e.g., as the effect of grafting or homopolymerization of IA. In that situation, the shift in the location of the peak of the carbonyl band towards higher wave numbers may result from the reduction in the amount of C=C groups coupled on the C=O group. The shift of the peak of the carbonyl band representing the carboxyl groups from 1703 to 1718 cm^{-1} , as observed by Yang and Gu during homopolymerization of IA, was explained by them in a similar way.¹⁸ On the other hand, the analyzed literature reports, on that subject, which describe degradation of carboxylic acids, indicate that the photo-oxidation process of low molecular weight and high molecular weight acids involves elimination of carboxyl groups,^{19–23} although that reaction does not need to be the dominant one.²¹ Photolysis of low molecular weight acids may follow the Norrish II mechanism, hence it may involve a reaction in which no radicals are formed.²³ However, the mechanism for photolysis of acrylic and methacrylic polyacids anticipates abstraction of the carboxyl group from the polymer backbone chain with the formation of a macro-radical and a carboxylic radical.^{19,21} Eventually, photolysis of the carboxylic group itself is also possible and likely.¹⁹

The reports provide also the information that carboxylic acids are not UV-sensitive, and those formed in the photo-degradation process will accumulate in the material.²⁴ From this point of view the changes in the band located at about 1700 cm^{-1} may result, on the other hand, from the increased content of carbonyl groups in acids and in ketones which were produced by the macromolecules oxidation process. Those changes, however, as measured at 1712 cm^{-1} were observed not earlier but after a few dozen hours of weathering [Fig. 2(a)]. Then, from the beginning of exposure to UV and over a few dozen hours, absorption was increasing for the component bands, within the wave numbers of 1730–1745 cm^{-1} and 1768–1780 cm^{-1} , which represented vibrations of carbonyl groups: in esters and in peracids/peresters, respectively. Despite no growth in the peak absorption for the carbonyl band (1712 cm^{-1}), the reported changes are indicative for oxidation of polymer macromolecules taking place from the very beginning of irradiation.

The profiles in Figure 2(a) reveal that, after initial clear increase in absorbance values for bands 1730–1745 cm^{-1} and 1768–1780 cm^{-1} , no significant changes could be observed over further dozens of hours of weathering. Absorption for the principal carbonyl band at 1712–1715 cm^{-1} started growing at the same time. After about 200 h, another growth was noted in intensity of the carbonyl band in esters

TABLE II
Absorption Bands Produced by Ageing of PE Grafted with KI

Band frequency, wave number (cm^{-1})	Type of vibrations of chemical functionality	Type of functional groups and structural fragments
3450	STR OH_{BOND}	Individual hydrogen bond in OH hydroxyl groups
3380	STR OH_{BOND}	Dual hydrogen bond in OH hydroxyl groups
1777 ^a	STR $\text{C}=\text{O}_{\text{PAC}}$	Carbonyl group in peracids/peresters
1739 ^a	STR $\text{C}=\text{O}_{\text{ES}}$	Carbonyl group in esters
1714 ^a	STR $\text{C}=\text{O}_{\text{AC+KET}}$	Carbonyl group in acids and ketones
1642	STR $\text{C}=\text{C}$	Unsaturated sites in macromolecules
1413	DEF $\text{CH}_2(\text{C}=\text{O}) + \text{BEND}_{\text{OH}}$	Methylene group located next to carbonyl group + in-plane bending vibrations in OH groups in acids, peracids and alcohols
1260	STR/ $\text{AS} \text{C}-\text{C}-\text{O}$	$\text{C}-\text{C}-\text{O}$ bond in acids, peracids and esters
1240	STR/ $\text{AS} \text{CH}_3-\text{C}-\text{O}$	Terminal (acetate) esters
1180	STR/ $\text{AS} \text{C}-\text{C}-\text{O}$	Intrachain esters
1082	STR $\text{C}-\text{C}-\text{O}$	Primary and secondary alcohols
993	WAG $\text{HC}=\text{CH}(\text{H})$	Terminal unsaturated sites (vinyl group)
967	WAG $\text{HC}=\text{CH}$	<i>Trans</i> -vinylene unsaturated sites
909	WAG $\text{OH} \cdots \text{O}_{\text{AC}} + \text{WAG}=\text{CH}_2$	Out-of-plane bending vibrations in OH groups in acid dimers

^a Wave numbers after deconvolution.

(1730–1745 cm^{-1}), and a bit later also for peroxide groups in acids and ketones (1768–1780 cm^{-1}). The intensity of changes in the former band was comparable to that observed for the principal carbonyl band.

The changes observed for the band at 3250–3580 cm^{-1} [Fig. 1(b)], which is specific for associated hydroxyl groups make another evidence for the fact that the polymer oxidation process was initiated from the very beginning of irradiation.^{24,25} Two peaks at 3380 and 3430 cm^{-1} became (poorly initially) visible within that region under irradiation conditions. At the end of weathering, absorbance for the latter wave number became dominant. Because of that, quantitative determinations within that spectral range were carried out for the peak value at 3430 cm^{-1} [Fig. 2(b)]. It should be pointed out here at the continual growth in the absorbance value over the whole test period, the growth being especially extensive at the early stage of weathering.

The band for isolated hydroxyl groups in hydroperoxides (at about 3555 cm^{-1}) is not sharply outlined [Fig. 1(b)]. That may result from low stability of those groups or from their low share. On the other hand, Lacoste and Carlson,²⁶ and also Gugumus,^{27,28} link associated hydroperoxides to the band with the peak at the wavelength of 3420–3410 cm^{-1} , i.e., within the spectrum subjected to analysis, for which a distinct growth in absorption was noticed in the weathering test.

The changes observed within the range of 1000–1100 cm^{-1} [Fig. 1(c)] confirm proper interpretation for the spectral range as described above. These are attributed to stretching vibrations of $\text{C}-\text{O}$ groups in primary and secondary alcohols and/or to deformation (bending) vibrations of $\text{C}-\text{O}-\text{H}$ and $\text{O}-\text{O}-\text{H}$ bonds in alcohols, peracids, and hydroperoxides.²⁹

The highest band observed in the weathering test within that range, with peak at 1080 cm^{-1} , is linked to stretching vibrations (STR/ $\text{A} \text{C}-\text{C}-\text{O}$) in primary and secondary alcohols.

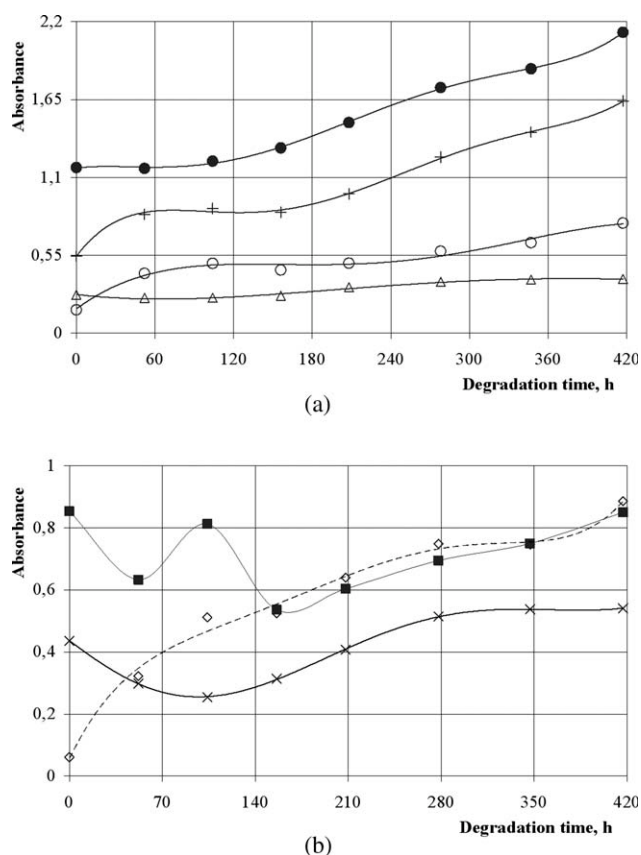


Figure 2 Changes in absorbance values of bands at selected wave numbers during photo-oxidative degradation of tested PE grafted with IA: (2a) (●) about 1712, (+) about 1730, (○) about 1780, and (△) about 1640 cm^{-1} , (2b) ■ 1216 cm^{-1} , ◇ 3430 cm^{-1} and × 910 cm^{-1} .

The changes were also observed in the spectrum of a sample after its weathering within wave numbers 1100–1400 cm^{-1} [Fig. 1(c)]. Authors of Ref. 30 suggest that the changes within that range result from the presence of compounds on the sample surface, such compounds coming from water which is sprinkled on samples within the weathering cycle (aluminum and silicon oxides). In our opinion, however, the bands appear in this range because of stretching vibrations of C—O bonds in various functional groups: in acids, peracids, esters, alcohols, and/or ethers. The bands disappeared which were specific for IA at 1216 cm^{-1} and 1170 cm^{-1} , as it was mentioned earlier and a new band appeared which became most intense within that range in time, at 1180–1182 cm^{-1} . That is characteristic for asymmetric stretching vibrations of $_{\text{STR/AS}}\text{C}^{\ominus}\text{—O—C}$ and $_{\text{STR/AS}}\text{C—C}^{\ominus}\text{—O}$ in intramolecular esters. Moreover, the maximum of the band 1309 cm^{-1} was shifted to 1300 cm^{-1} with no essential change in its intensity. That band makes the consequence of deformation vibrations of CH_2 groups in the PE amorphous phase. After a few dozen hours of weathering, two more small bands appeared: at 1240 cm^{-1} (more clearly outlined) and a neighboring one at 1260 cm^{-1} . The first one most probably represents stretching vibrations in $\text{CH}_3\text{—C}^{\ominus}\text{—O}$ groups of terminal esters ($\text{CH}_3\text{—C(O)—OR}$ acetates). That may be additionally confirmed by the increase of the band at 1375 cm^{-1} which is specific for scissoring vibrations in CH_3 groups located close to the carbonyl group coal atom ($_{\text{SCI}}\text{CH}_3(\text{C=O})$). Those vibrations are visible in the spectrum close to the band at 1378 cm^{-1} , which is typical for CH_3 groups in the PE hydrocarbon chain. Further, the band at 1260 cm^{-1} is surely the effect of overlapping two other bands: stretching vibrations of $_{\text{STR}}\text{C}^{\ominus}\text{—O}$, $_{\text{STR/AS}}\text{C—C}^{\ominus}\text{—O}$ in acids (1260–1280 cm^{-1}) as well as in peracids and preesters (1250–1270 cm^{-1}). It is worth mentioning here that esters, the presence of which is confirmed by spectral changes, may be produced not only in radical processes. They may probably be formed in condensation reactions of carboxyl groups in grafted IA and free IA with primary and secondary alcohols which are formed from the very beginning of the ageing process.^{31,32}

In the vicinity of the range of wave numbers as discussed above, there was also a band with maximum 1409 cm^{-1} , which shifted to 1413 cm^{-1} over the weathering process, increasing somewhat its intensity at the same time. That band may be explained by deformation vibrations of OH groups in acids ($_{\text{DEF}}\text{OH}_{\text{AC}}$) and of $\text{—CH}_2(\text{C}^{\ominus})$ groups in esters, acids, and ketones. Similarly, Yang and Gu¹⁸ observed a band moving from 1400 to 1415 cm^{-1} in the IA homopolymerization process. They attributed that band to the combination of stretching vibrations

of C—O bond and deformation vibrations of —O—H in dimers of unsaturated acids, and after the shift of the band—of saturated acids. The authors of Ref. 25 suggest that the changes in the discussed spectral region represent changes within carbonyl groups which are located close to CH_2 groups.

Irrespective of changes in absorbances for oxygen-containing groups, after a few dozen hours of weathering, a band with maximum at 1642 cm^{-1} appeared in the spectrum [Fig. 1(a)]; that represented the growing amount of unsaturated groups C=C in the polymer. Changes were also observed within lower wave numbers, where initial decline in absorbance took place of the most intense band at 916 cm^{-1} [Fig. 1(c)], which represented wagging vibrations of —OH groups in acid dimers $_{\text{WAG}}\text{OH—O}_{\text{AC}}$ and $_{\text{WAG}}\text{=CH}_2$ of IA. Additionally, formation of a new and equally intense band was observed, with maximum at 909 cm^{-1} , which was specific for unsaturated vinyl groups HC=CH_2 created within the polymer. That band is attributed to terminal unsaturated groups.^{29,33,34} Another adjacent band was seen permanently in the spectrum, at 889 cm^{-1} , for the same vibrations $_{\text{WAG}}\text{=CH}_2$ but in vinylidene groups >C=CH_2 , as well as one more band at 967 cm^{-1} ($_{\text{WAG}}\text{CH=CH}$) for *trans*-vinylene groups. Irradiation created additionally yet another band at 990 cm^{-1} , with low intensity, which represented vibrations $_{\text{WAG}}\text{CH=CH(H)}$ within vinyl groups.

Quantitative determinations were carried out at the wave number of 909 cm^{-1} , at the location of maximum for the most intense band of that range [Fig. 2(b)]. Another indication of changes within unsaturated groups C=C of the polymer was based on the measurements of absorbance for the $_{\text{STR}}\text{C=C}$ band at 1642 cm^{-1} [Fig. 2(a)]. It should be mentioned that both those bands offered the lowest intensity over the whole period of ageing, as referred to all bands subjected to quantitative analysis.

Because of the complex nature of the spectrum within some analyzed ranges, and because of shifts of specific band peaks as a result of the ageing process, the analysis of changes in band absorbances at specific wave numbers as described above was supplemented also by determination of changes in band areas within selected spectral ranges. That procedure allows for simultaneous consideration of all components of the investigated bands in the quantitative analysis, i.e., consideration will be given to all groups which have absorption bands within the spectral range studied. Measurements were taken within two ranges: within the carbonyl range from 1600 to 1870 cm^{-1} , which corresponds to the so-called carbonyl index, and within the hydroxyl range from 3260 to 3580 cm^{-1} , which makes a basis for the hydroxyl index. Each of them is

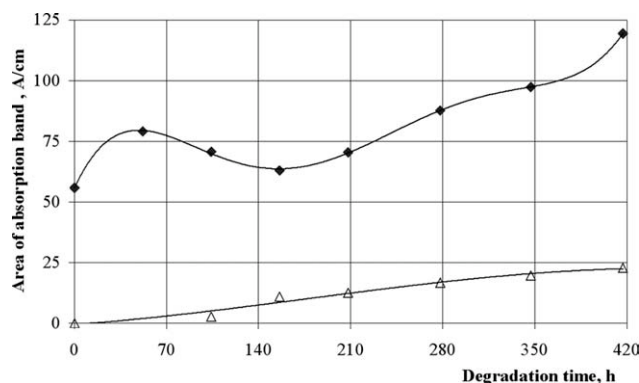


Figure 3 Changes in surface areas versus photo-oxidative ageing time, for absorption bands in selected spectral ranges. Sample: for PE grafted with IA. \blacklozenge carbonyl index (surface area below the absorption band for carbonyl groups $1600\text{--}1870\text{ cm}^{-1}$), \triangle hydroxyl index (surface area below the absorption band for hydroxyl groups $3547\text{--}3285\text{ cm}^{-1}$)

acknowledged as a measure for the progress of the polymer oxidation process (Fig. 3). As can be seen, a gradual increase of the hydroxyl index was observed from the very beginning of the ageing process, in contrast to the complex profile of changes for the carbonyl index. The profile for the latter clearly climbs up initially, then it goes down, and finally its stable increase is noted. Reduction in the area of the carbonyl band under irradiation of poly(acrylic acid) was also reported in Ref. 22. That was claimed to result from destruction or separation carbonyl groups from polymer chains. It should be noted that the observed profile of changes in the carbonyl band area does not correlate with the change in absorbance which was measured for the peak in that band at 1712 cm^{-1} as described earlier [Fig. 2(a)]. To clarify that discrepancy, the spectral range of $1600\text{--}1870\text{ cm}^{-1}$ was subjected to computer-aided deconvolution (Fig. 4). The adopted procedure made it

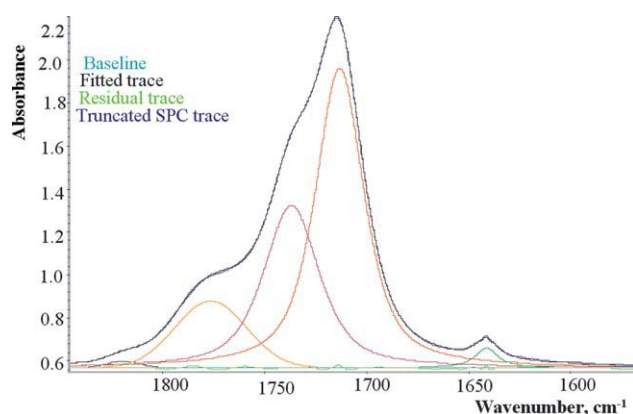


Figure 4 Deconvolution of the range $1870\text{--}1600\text{ cm}^{-1}$ in the FTIR spectrum into component bands for the PE sample after exposure of 347 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

possible to isolate carbonyl bands from the spectrum which were specific for acids and ketones ($1712\text{--}1718\text{ cm}^{-1}$), for esters ($1736\text{--}1744\text{ cm}^{-1}$), and for peroxide forms in acids and esters ($1771\text{--}1780\text{ cm}^{-1}$). These were identical to those identified during preliminary analysis of the spectrum. The band for unsaturated groups ($1630\text{--}1641\text{ cm}^{-1}$) made the additional component in that range. Determination of surface areas for component bands suggested the highest share of acid-derived and ketone-derived carbonyl groups ($1712\text{--}1718\text{ cm}^{-1}$) in the material subjected to ageing. The nature of changes which were observed within that range (Fig. 5), at least at the initial stage of ageing, was clearly different from the absorbance profile as recorded for the initial spectrum at 1712 cm^{-1} [Fig. 2(a)] and it was closer to the carbonyl index profile (Fig. 3). As can be seen in Figure 5, the first dose of irradiation increased the area of the analyzed band, which probably resulted from the initiation of the polymer photo-oxidation process. Then, a considerable reduction was observed in the band surface area, which may result from the changes within the carboxyl group band as described earlier.²² Not earlier than after about 150 h of irradiation, the surface area of the analyzed band revealed the successive and regular growth (Fig. 5). A similar character of changes in the surface area was found (Fig. 5) for the selected band of peresters and peracids ($1771\text{--}1780\text{ cm}^{-1}$), although it was clearly less intense. Yet less intense changes, but with the similar profile, were observed for the unsaturated group band ($1630\text{--}1641\text{ cm}^{-1}$). And then, the surface area for the band representing carbonyl groups in esters ($1736\text{--}1744\text{ cm}^{-1}$) started growing in parallel with the lowering of the ketone and acid band ($1712\text{--}1718\text{ cm}^{-1}$). After a short period of slow down in changes (in parallel to the behavior of changes noted within the ketone and acid bands),

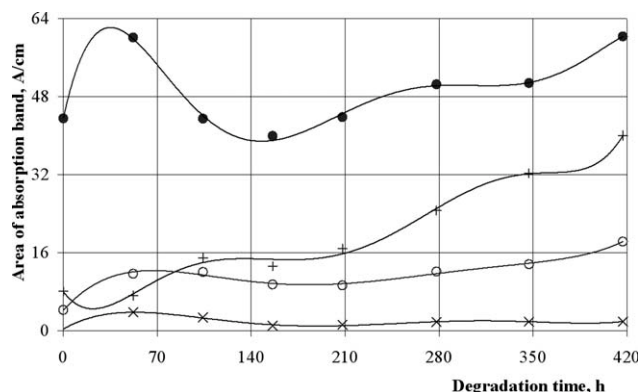


Figure 5 Surface area values for bands after deconvolution of the spectrum within $1600\text{--}1870\text{ cm}^{-1}$ into component bands, versus ageing time: (●) carbonyl groups in acids and ketones ($1718\text{--}1712\text{ cm}^{-1}$), (+) ester groups ($1744\text{--}1736\text{ cm}^{-1}$), (○) perester and peracid groups ($1771\text{--}1780\text{ cm}^{-1}$), (×) unsaturated groups ($1630\text{--}1641\text{ cm}^{-1}$).

TABLE III
Changes in Distribution of Molecular Weight (MWD), Gel Number, and Density of Plastic During Photo-Oxidative Ageing of Polyethylene Grafted with Itaconic Acid

Parameter	Ageing time (h)							
	0	52	104	156	208	278	347	417
MWD	7	7	6	5	7	6	8	5
Gel number, (cg/g)	1.5	nd	nd	nd	nd	nd	nd	11
Density (g/cm ³)	0.933	nd	nd	nd	nd	nd	nd	0.935

nd, not determined.

another stable increase was observed in the ester band which accompanied similar changes within the carbonyl band for acids and ketones. When the profiles in Figure 5 are compared with each other, the share of esters turns out to grow a bit faster than that of acids and ketones.

Attention should be paid to the fact that the character of the observed absorbance changes at 1780 cm⁻¹ [Fig. 2(a)] is nearly the same as that of the curve for the changes in the surface area of the respective separated band (Fig. 5). Similar consistence was noted for the band at 1630–1641 cm⁻¹. One may thus conclude that the wave number values, for which absorbances were measured, are representative for the groups, the presence of which is decisive for intensity of the analyzed band. On the other hand, the profiles for the curves which show the changes in absorbances and in surface areas for the carbonyl band of esters (1736–1744 cm⁻¹) as well as of ketones and acids (1712–1718 cm⁻¹) are different [Figs. 2(a) and 5]. The reason can be perceived in a high variety of intra- and intermolecular interactions, which also involve carboxyl groups in the modifying agent, which means considerable diversification of existing and new fragment (produced in the ageing process) which contain carbonyl groups. As a consequence, it is good to utilize both procedures for the analysis of FTIR spectra when studying the oxidation process of functionalized polymers, to present complexity of the reactions which take place.

The summary of all test results leads to a general conclusion that the oxidation process of PE grafted with IA involved no induction period, i.e., it started from the very beginning of irradiation. Carbonyl groups made the principal products of that process, and these were located within the structures of ketones, acids, and esters (inclusive of their peroxide forms). Hydroxyl groups made the second essential group of products, and those groups made structural elements of alcohols and hydroperoxides. The share of unsaturated groups C=C was relatively small.

Molecular changes in samples under ageing

After the weathering tests were finished, the samples were subjected to analysis for the contents of cross-

linked fractions (gel number). The oxidation process of IA-grafted PE was found to be accompanied by sample crosslinking; that resulted from intermolecular recombination of macro-radicals produced in the ageing process (Table III). Additionally, a small increase of the polymer molecular weight was observed at the first stage of ageing (Fig. 6), which may be confirmation for the crosslinking process. No changes in the polymer density were found (Table III) which is indicative for a relatively small share of the crosslinking process *versus* oxidation reactions.

Reduction of the polymer molecular weight, as observed at successive stages of the ageing process (Fig. 6) suggests in turn that polymer macromolecules were breaking down during oxidation, and that process covered all molecule sizes (small changes is MWD—Table III). The data shown in Figure 6 are indicative for the correlation between changes in molecular weights (especially M_n) and changes in polymer oxidation intensity as measured by absorbance at 1712 cm⁻¹. Hence, the changes in said band are representative for breaking polymer macromolecules, irrespective of whether the changes are attributable to changes in polymer ketone groups or in polymer carboxyl groups.

CONCLUSIONS

PE grafted with IA was subjected to weathering in laboratory test. The presence of intense bands

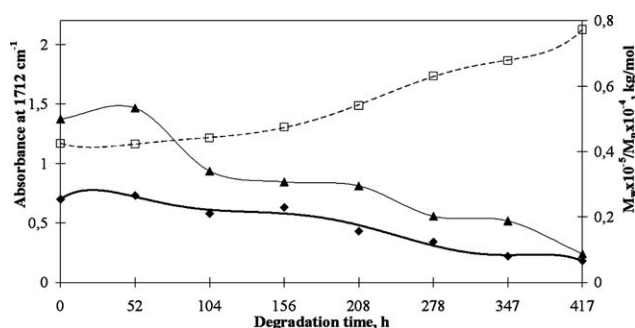


Figure 6 Changes in the weight average (▲) and number average (◆) molecular weights, and in absorbance of the carbonyl band (□) at the wave number 1712 cm⁻¹ *versus* ageing time. Sample: PE grafted with IA.

derived from the modifier functional groups in the FTIR spectrum of the tested polymer made it harder to evaluate the progress of the polymer oxidation process. It was found reasonable to analyze the course of the ageing process for a modified polymer both through quantitative measurements of changes in absorbance values at selected wave numbers and through measurements of surface area values for absorption bands which were separated by means of deconvolution. The use of both those procedures of quantitative determinations resulted in a general conclusion that the oxidation process was initiated from the very first moment of irradiation, and it produced ketones, acids, esters (intramolecular and of acetate type), peracids, peresters, hydroperoxides, and alcohols. Small changes were observed only within the bands which are specific for unsaturated groups C=C. Oxidation was accompanied by cracking of polymer macromolecules. Some limited polymer crosslinking was observed, too.

The obtained results show that low-density PE grafted with IA is sensitive to UV radiation, which may cause degradation of that material under natural conditions. That conclusion should be finally confirmed by weathering tests conducted under natural conditions.

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